Supporting Information for:

New Insights into the Mechanism of Ruthenium Catalyzed Olefin Metathesis Reactions

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Experimental Section:

General Procedures: Manipulation of organometallic compounds was performed using standard Schlenk techniques under an atmosphere of dry argon or in a nitrogen-filled Vacuum Atmospheres drybox (O_2 < 2 ppm). Toluene-d_8 was degassed using three consecutive freeze-pump-thaw cycles and vacuum transferred from Na/benzophenone. PCy_3 was obtained from Strem Chemicals and used as received. All vinyl ether substrates were obtained from Aldrich and were dried over CaH_2. Complex **1** was prepared according to literature procedures.[1]

NMR spectra were recorded on a Varian Inova (499.852 MHz for ^1H; 202.338 MHz for ^{31}P) or a Varian Mercury 300 (299.817 for ^1H). ^{31}P NMR specra were referenced using H_3PO_4 (δ = 0 ppm) as an external standard. UV-Vis spectra were recorded on an HP 8452A Diode Array Spectrophotometer.

Preparation of $IMesH_2(PCy_3)(Cl)_2Ru{=}CHPh$ (2). Complex **2** was prepared by a modification of the literature procedure.[2] 1,3-dimesityl-4,5-dihydroimidazolium tetrafluoroborate (0.90 g, 2.7 mmol) and KO^{t}Bu (0.30 g, 2.7 mmol) were combined in THF (20 mL). The resulting suspension was stirred at room temperature for 1 hour. To this suspension was added a solution of **1** (1.1 g, 1.3 mmol) in C_6H_6 (20 mL), and the resulting purple suspension was refluxed for 30 minutes during which time a color change to brown-red was observed. The solvent was removed completely under vacuum, and the resulting reddish solids were dissolved in C_6H_6 (30 mL) and filtered through a plug of Celite. The red solution was concentrated to about 3 mL and methanol (45 mL) was added to precipitate the desired product. The product was cannula filtered and washed with 3 x 30 mL of methanol and 2 x 10 mL of pentane. The resulting pinkish-red solids were dried under vacuum to afford 0.50 g (45 % yield of the product).

Magnetization Transfer Experiments: The appropriate ruthenium alkylidene (0.024 mmol) and PCy_3 (in equivalents relative to [Ru]) were combined in toluene-d_8 (600 μL) in a screw cap NMR tube, and the resulting solution was allowed to

thermally equilibrate in the NMR probe. The free phosphine resonance was selectively inverted using the DANTE[3] pulse sequence and after variable mixing times (between 0.00003 and 50 s), a non-selective 90° pulse was applied and an FID recorded. ^{1}H decoupling was applied during the 90° pulse. In both cases, spectra were collected as 4-8 transients with relaxation delays between 30 and 50 seconds. The peak heights of the free and bound phosphine at variable mixing times were analyzed using the computer program CIFIT[4] in order to obtain the exchange rate of bound phosphine with free phosphine (k_B). Values for the T_1's for the free and bound phosphine were also obtained in this analysis, and the results are summaried in Table S1. Sample fits of the experimental data (complex **1** with 3 eq PCy_3 at 70 °C) for free and bound phosphine shown in Figures S1 and S2 respectively. Eyring plots for phosphine exchange in complexes **1** and **2** are shown in Figures S3 and S4. The relaxation times (T_1) for complexes **1** and **2** and for free PCy_3 were determined independently (at 50 °C in toluene-d_8) using standard inversion recovery experiments and the results are summarized in Table S2.

NMR Kinetics of Initiation Reactions: The ruthenium alkylidene (0.0106 mmol) was dissolved in toluene-d_8 (600 μL) in a screw cap NMR tube. The resulting solution was allowed to equilibrate in the NMR probe at the appropriate temperature (10 °C for **1** and 35 °C for **2**). Substrate (in equivalents relative to [Ru]) was injected into the NMR tube neat. Reactions were monitored by measuring the peak heights of the starting alkylidene as a function of time over at least three half lives. The data was fitted to a first order exponential using Varian kinetics software.[5] The observed pseudo first order rate constants are summarized in Table S3. A sample of the experimental data (with the first order exponential fit) is shown in Figure S5.

UV-Vis Kinetics: In a cuvette fitted with a rubber septum, a solution of ethyl vinyl ether (in equivalents relative to the [Ru]) in toluene (1.6 mL) was prepared. This solution was allowed to thermally equilibrate in the UV-Vis spectrometer at 20 °C. To the temperature equilibrated solution was added 100 μL of a 0.0139 M stock solution of **1** in toluene. The kinetics of the reaction were followed by monitoring the appearance of the product at 484 nm. The data was collected over 5 half lives and kinetics traces were fitted to a first order exponential. The observed pseudo first order rate constants are summarized in Table S4, and a sample exponential fit of the experimental data is shown in Figure S6.

Phosphine Dependence Experiments for Determining k_{-1}/k_2 in Complex 1. Alkylidene **1** (0.0106 mmol) and PCy_3 (0.0014 mmol, 0.0027 mmol,

0.0053 mmol and 0.0080 mmol from a freshly prepared 0.061 M stock solution in toluene-d_8) were combined in four separate Screw cap NMR tubes. The resulting solutions were diluted to a total volume of 600 total μL of toluene-d_8. The tubes were allowed to thermally equilibrate at 37 °C in the NMR probe, and the vinyl ether substrate (ethyl vinyl ether, 0.318 mmol) was injected neat into the NMR tube. Reactions were monitored by measuring the peak heights of the starting alkylidene as a function of time over at least three half lives as described above. The resulting data are summarized in Table S5. A plot of $1/k_{obs}$ as a function of [PCy_3]/[olefin] for complex **1** is shown in Figure S7.

Phosphine Dependence Experiments for Determining k_{-1}/k_2 in Complex 2. Alkylidene **2** (0.0106 mmol) and PCy_3 (0.0178 mmol, 0.0571 mmol, 0.107 mmol, 0.232 mmol, and 0.335 mmol) were combined in five separate Screw cap NMR tubes. The solids were dissolved 600 total μL of toluene-d_8. Each solution was allowed to thermally equilibrate at 50 °C in the NMR probe, and the vinyl ether substrate (ethyl vinyl ether, 0.146 mmol) was injected neat into the NMR tube. Reactions were monitored by measuring the peak heights of the starting alkylidene as a function of time over at least three half lives as described above. The resulting data are summarized in Table S6. A plot of $1/k_{obs}$ as a function of [PCy_3]/[olefin] for complex **2** is shown in Figure S8.

Table S1. Observed Rate Constants for Phosphine Exchange in Complexes **1** and **2**.

Complex	k_B/s^{-1}	eq PR_3	T/K	T_{1F}/s	T_{1C}/s
1	0.116±0.006	3 eq	313	9.2	2.3
1	0.381±0.01	3 eq	323	9.8	2.7
1	1.21±0.02	3 eq	333	8.9	3.1
1	3.56±0.06	3 eq	343	7.8	3.6
1	9.57±0.06	3 eq	353	7.3	4.3
1	1.22±0.04	1.5 eq	333	8.3	3.3
1	1.13±0.04	10 eq	333	10.0	2.7
1	1.11±0.03	20 eq	333	9.0	2.3
2	0.04±0.01	1.5 eq	343	4.9	3.4
2	0.126±0.006	1.5 eq	353	8.4	3.6
2	0.355±0.016	1.5 eq	363	7.4	3.9
2	1.02±0.06	1.5 eq	373	12.6	3.4
2	0.121±0.08	5 eq	353	10.5	3.7
2	0.12±0.02	10 eq	353	9.2	3.3

Table S2. T_1 Analysis for complexes **1** and **2** (50 °C in C_7D_8)

Complex	T_1 (s^{-1})
PCy_3	11.1±0.2
1	2.46±0.02
2	3.07±0.06

Table S3. Rate Constants for Reaction of Complexes **1** (at 35 °C) and **2** (at 10 °C) with Vinyl Ether Substrates (^{1}H NMR Spectroscopy)

Complex	Substrate (Eq)	k_{obs} (s^{-1})
1	Ethyl vinyl ether (30 eq)	1.2×10^{-3}
1	Ethyl vinyl ether (45 eq)	1.5×10^{-3}
1	Ethyl vinyl ether (60 eq)	1.7×10^{-3}
1	Ethyl vinyl ether (120 eq)	2.2×10^{-3}
2	Ethyl vinyl ether (5 eq)	4.5×10^{-4}
2	Ethyl vinyl ether (15 eq)	4.5×10^{-4}
2	Ethyl vinyl ether (30 eq)	4.6×10^{-4}
2	Ethyl vinyl ether (45 eq)	4.6×10^{-4}
2	Ethyl vinyl ether (60 eq)	4.8×10^{-4}
2	2, 3 Dihydrofuran (5 eq)	4.5×10^{-4}
2	2, 3 Dihydrofuran (15 eq)	4.4×10^{-4}
2	2, 3 Dihydrofuran (30 eq)	4.6×10^{-4}
2	Ethyl 1-propenyl ether (5 eq)	4.5×10^{-4}
2	Ethyl 1-propenyl ether (15 eq)	4.5×10^{-4}
2	Ethyl 1-propenyl ether (30 eq)	4.9×10^{-4}

Table S4. Rate Constants for Reaction of Complex **2** (20 °C) with Ethyl Vinyl Ether (UV-Vis Spectroscopy)

Complex	Substrate (Eq)	k_{obs} (s^{-1})
1	Ethyl vinyl ether (755 eq)	0.016±0.001
1	Ethyl vinyl ether (1880 eq)	0.018±0.001
1	Ethyl vinyl ether (5300 eq)	0.018±0.001

Table S5. $[PCy_3]/[Olefin]$ Experiments for **1**.

Complex	mmol PCy_3	$[PCy_3]/[olefin]$	$1/k_{obs}$
1	0.0014	0.0044	421
1	0.0027	0.0085	800
1	0.0053	0.017	1582
1	0.0080	0.025	2398

Table S6. $[PCy_3]/[Olefin]$ Experiments for **2**.

Complex	mmol PCy_3	$[PCy_3]/[olefin]$	$1/k_{obs}$
2	0.0178	0.112	353
2	0.0571	0.391	534
2	0.107	0.733	629
2	0.232	1.59	959
2	0.335	2.29	1300

References

1. Schwab, P.; Grubbs, R.H.; Ziller, J.W. *J. Am. Chem. Soc.* **1996**, *118*, 100.
2. Scholl, M.; Ding, S.; Lee, C.W.; Grubbs, R.H. *Org. Lett.* **1999**, *1*, 953.
3. Morris, G.A.; Freeman, R. *J. Magn. Res.* **1978**, *29*, 433.
4. Bain, A.D.; Kramer, J.A. *J. Magn. Res.* **1996**, *118A*, 21.
5. VNMR 6.1B Software, Varian Associates, Inc.

Figure S1. Free Phosphine Magnetization Transfer Data

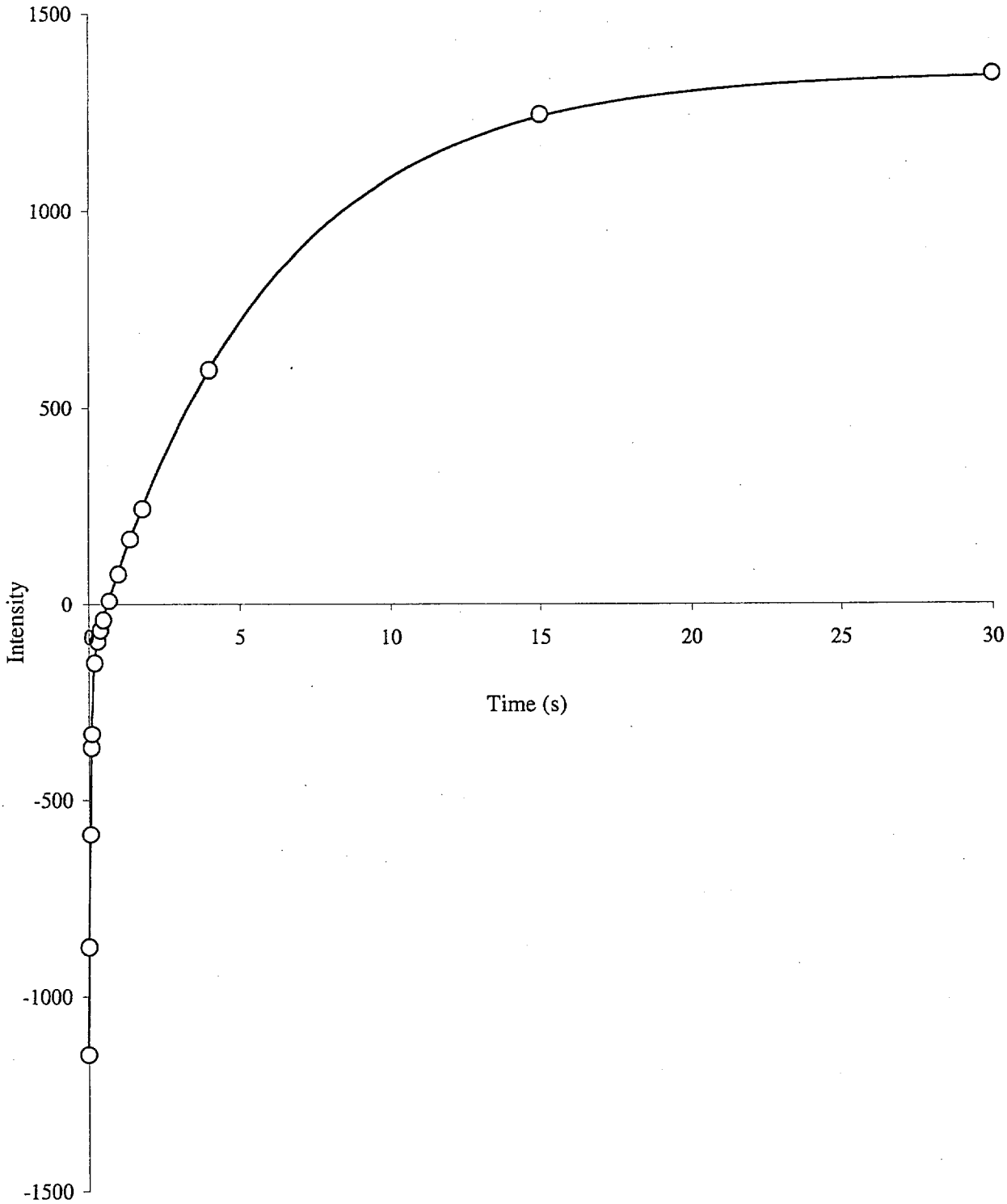

Figure S2. Bound Phosphine Magnetization Transfer Data

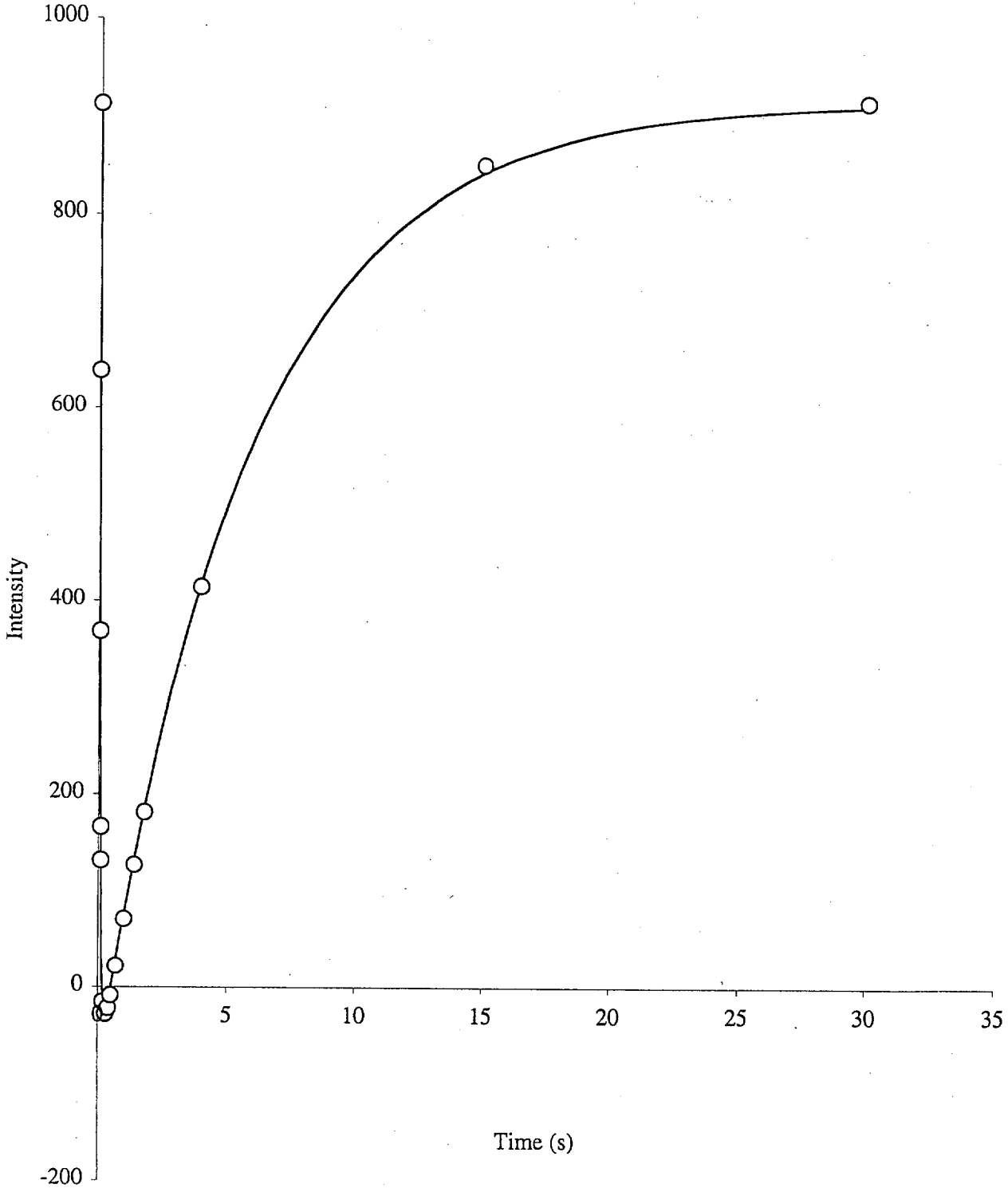

Figure S3. Eyring Plot for Complex 1

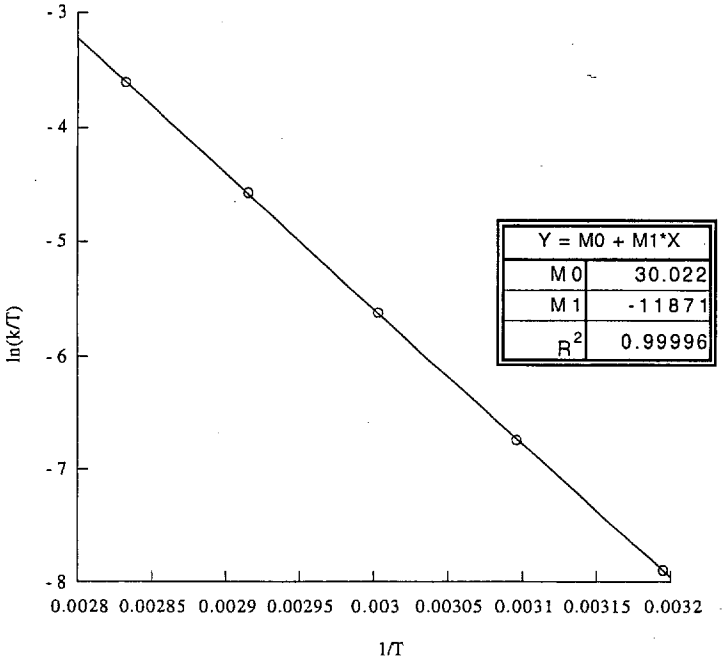

Figure S4. Eyring Plot for Complex 2

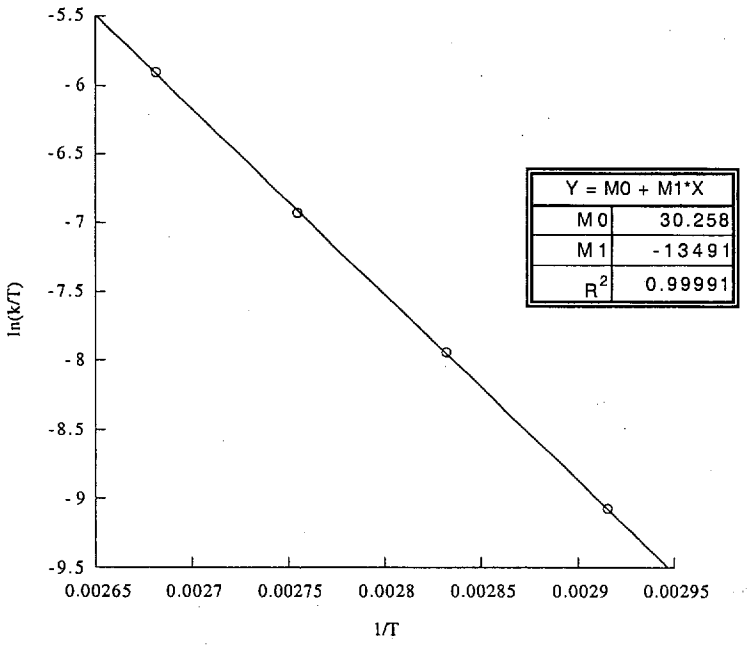

Figure S5. NMR Kinetics for Reaction of 2 with 15 eq Ethyl Vinyl Ether

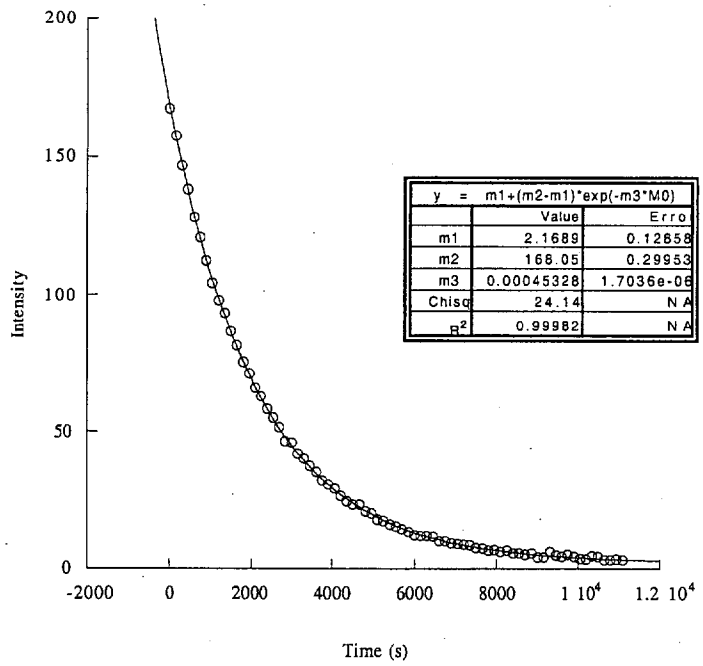

Figure S6. UV-Vis Kinetics for Reaction of 1 with 755 eq Ethyl Vinyl Ether

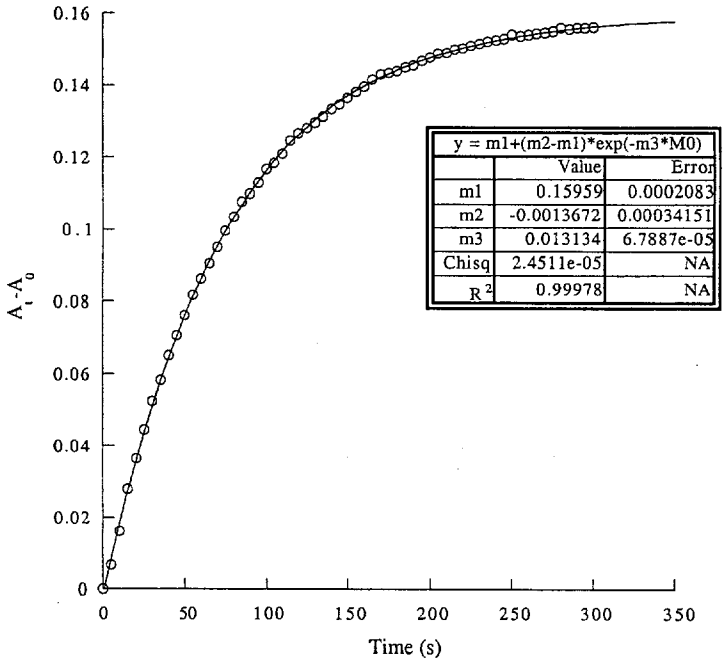

Figure S7. $1/k_{obs}$ versus $[PCy_3]/[Olefin]$ for Complex 1

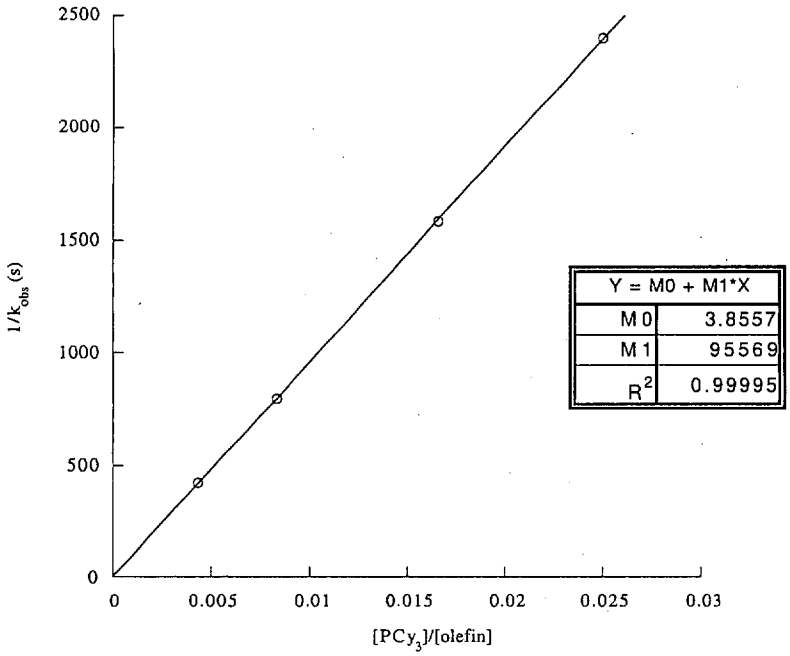

Figure S8. $1/k_{obs}$ versus $[PCy_3]/[olefin]$ for Complex 2